

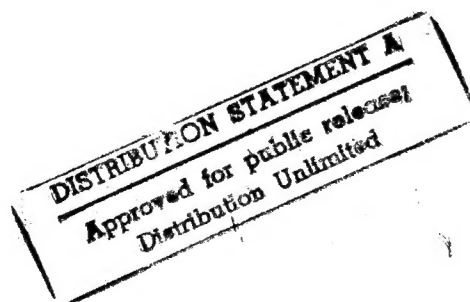


# Structure of Ordinary Ice $I_h$

## Part I: Ideal Structure of Ice

Victor F. Petrenko

October 1993



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**Abstract**

This report examines the defect-free structure of ordinary  $I_h$ , reviewing experimental results and theoretical models of the arrangement of oxygen and hydrogen atoms and the electronic structure of ice. Special attention is given to the results of studies from the last two decades. Among the experimental techniques under consideration are X-ray diffraction, optical absorption, X-ray photoelectron spectroscopy and ultraviolet optical spectroscopy, nuclear magnetic resonance and electron spin resonance. The main subjects discussed are the chemical content of ice, the structure and properties of water molecules, hydrogen bonds, phase transitions, protonic disorder and electron energy spectrum of ice.

For conversion of SI metric units to U.S./British customary units of measurement consult *Standard Practice for Use of the International System of Units (SI)*, ASTM Standard E380-89a, published by the American Society for Testing and Materials, 1916 Race St., Philadelphia, Pa. 19103.

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**US Army Corps  
of Engineers**

Cold Regions Research &  
Engineering Laboratory

## **Structure of Ordinary Ice $I_h$** **Part I: Ideal Structure of Ice**

Victor F. Petrenko

October 1993

DTIC QUALITY INSPECTED 5

Prepared in cooperation with  
THAYER SCHOOL OF ENGINEERING  
DARTMOUTH COLLEGE



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## PREFACE

This report was prepared by Dr. Victor F. Petrenko, Professor of Engineering, Thayer School of Engineering, Dartmouth College, Hanover, New Hampshire. Funding was provided by the U.S. Army Research Office through contract DAAL 03-91-G-0164.

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## FOREWORD

At the present time, thousands and thousands of people around the world deal with ice, snow and permafrost. They are scientists, educators, engineers, navigators, meteorologists and others. While a small fraction of these people contribute to the knowledge base in ice physics, all of them use knowledge from it frequently. Moreover, successful applied research is based upon fundamental science—one more reason for ice specialists to have a textbook on ice physics on their desks.

The first modern ice physics text was Fletcher's book on *The Chemical Physics of Ice* (1970). Fletcher's book is in typical textbook format: it is reasonably brief and easy to understand. He touched on a few of the most important topics, but not all of them.

The most comprehensive book on ice physics to date was published by Hobbs in 1974. Hobbs considered almost all of the basic aspects of ice as understood at that time. Moreover, he described and compared several (sometimes opposing) viewpoints. This fundamental and rather large (837 pages) book is commonly known as the "Ice Bible" by specialists in the field. In 1974 and 1975, two monographs on ice were produced by John Glen. These were briefly and clearly written and reviewed almost all ice-related subjects. This work was (and in some respects still is) a magnificent introduction to ice.

Finally, in 1981 Maeno wrote a simple popular book for the express purpose of attracting people's attention to the subject.

During the past 20 years, a significant amount of new experimental and theoretical work has appeared, dramatically changing our views on ice physics. As a result, we are now able to formulate physical laws using more simple and direct methods. We have found some of the physical models used in the past to be completely wrong. The physics of ice is a much better developed subject than it was 20 years ago.

For the above reasons, we feel the time is ripe for a contemporary book on ice physics, incorporating the known and proven with almost 20 years worth of material not covered by previous works.

I have tried to prepare a "readable" book, and not one that requires the reader to be a uniquely educated person. It is my intent to present the material in such a way that any reader attracted by the title *Ice Physics* will be able to comprehend it. This is quite difficult for a book dedicated, not to a particular field of knowledge, but to a specific material. Indeed, for ice it means we have to consider a wide variety of subjects, including quantum chemistry, solid state physics, the theory of elasticity, ionic conductivity, synchrotron X-ray topography, crystal growth, the physics of surfaces and more.

The primary goal is to produce as simple a book as possible without sacrificing scientific accuracy. Experimental facts, physical ideas and theories will be strongly organized and bound together cohesively. The reader will be introduced to a wide variety of material on a step by step basis. Then the picture will be whole.

To accelerate materials publication, this book will appear first in the form of a series of joint CRREL-Dartmouth reports, later to be published in CRREL's Monograph series, on:

1. The structure of ordinary ice
  - Part I: "Ideal" structure of ice. Ice crystal lattice
  - Part II: Real structure of ice. Defects

2. Electrical properties of ice
  - Part I: Conductivity and dielectric permittivity of ice
  - Part II: Advanced topics and new physical phenomena
3. Optical properties
4. Electro-optical effects in ice
5. Thermal properties
6. Mechanical properties of ice. Elasticity and anelastic relaxation. Plastic properties. Fracture of ice
7. Electromechanical effects in ice
8. Surface of ice
9. Other forms of ice and their properties
10. Ice in space
11. Ice research laboratories

The reports will be prepared in a sequence convenient to the author. The present report is the second in the series.



# Structure of Ordinary Ice $I_h$

## Part I : Ideal Structure of Ice

VICTOR F. PETRENKO

### INTRODUCTION

Unlike most of the preceding books and monographs on ice physics (Fletcher 1970, Glen 1974, Hobbs 1974), this report will be concerned only with the structure of ordinary ice  $I_h$ . The structures of numerous other forms of ice, which exist either at very high pressures or very low temperatures, will be considered in a later report. I have chosen such an approach because the overwhelming majority of people interested in ice deal with ordinary hexagonal ice  $I_h$ .

The other essential difference in the description of ice structure is the separate treatment of "ideal" or defectless structure and "real" structure. Such a division reflects, first, the important role that defects play in materials physics. Second, it is in the study of defects (dislocations, point defects, grain boundaries) that significant progress has been achieved since the last monograph on ice physics was published.

A new topic for books about ice will be a section describing the structure of electron energy bands in ice—this is currently a frontier of theoretical and experimental investigations in ice physics. Lattice elastic vibrations—phonons—will be discussed in the report devoted to the thermal properties of ice.

### CHEMICAL CONTENT OF WATER AND ICE—IMPURITIES AND ISOTOPES

Let us consider briefly some basic properties of liquid water prior to analyzing ice structure. First, water is directly present in many of the instances that we are going to discuss: for example, when ice is growing from a melt or when ice is melting and water is present at the ice surface in the form of a thin film.

Second, many physical properties of ice and water are similar. This is attributable to water being a molecular liquid and ice being a molecular crystal. The fact that water molecules in these substances preserve their individuality determines, for instance, some of the optical and thermal properties. In those cases of some major difference in the behavior of water and ice, this gives a key to understanding the mechanism of the phenomenon, since the structural distinctions between ice and water can be formulated quite accurately.

There is no point in proving to the reader that water consists of oxygen and hydrogen, since we acquire this knowledge in high school. One of the most simple and accessible ways to determine the chemical content of water is via electrolysis. I believe that many readers successfully performed this simple experiment back in their childhood. By measuring the volumes of gases generated in the electrolysis process



and using Avogadro's law, we can establish the chemical formula of water:  $\text{H}_2\text{O}$ . One should keep in mind, however, that the path to understanding this at-first-glance simple result was tiresome and difficult. Major contributions to this research were made by such famous scientists as Cavendish, Lavoisier, Dalton and Avogadro. Water is a strong and fairly versatile solvent. Therefore, water found in nature usually contains substantial amounts of various salts, gases and organic compounds in dissolved form. Owing to the high solubility of oxygen in water, thousands of diverse animals live in seas, rivers and lakes.

**Table 1. Physical properties of ordinary (H<sub>2</sub>O) and heavy (D<sub>2</sub>O) water (after Malenkov 1988).**

Parameter	H <sub>2</sub> O	D <sub>2</sub> O
Density		
ice at 0°C	0.917 g/cm <sup>3</sup>	1.017 g/cm <sup>3</sup>
liquid at 20°C	0.9982 g/cm <sup>3</sup>	1.1053 g/cm <sup>3</sup>
Viscosity at 20°C	1.005 c	1.251 c
Melting point	273.16 K (0°C)	276.97 K (3.815°C)
Boiling point	373.16 K (100°C)	374.59 K (101.43°C)
Critical temperature	647.3 K (374.15°C)	643.9 K (370.7 °C)
Critical pressure	22.06 MPa	21.67 MPa
Critical density	0.322 g/cm <sup>3</sup>	0.356 g/cm <sup>3</sup>
Latent heat of fusion	332.4 J/g	316.6 J/g
Latent heat of vaporation	2256.2 J/g	2070.9 J/g
Latent heat of sublimation of ice at 0°C	2833.9 J/g	2639.6 J/g
Specific heat capacity (c <sub>p</sub> )		
ice at 0°C	2.038 J/g K	2.202 J/g K
liquid at 0°C	4.186 J/g K	4.23 J/g K
vapor at 0°C	1.905 J/g K	1.68 J/g K
Dielectric permittivity		
ice at -10°C	95	92
liquid at 25°C	78.54	78.25
Thermal conductivity		
ice at 0°C	234.6 mW/m K	—
liquid at 0°C	560.9 mW/m K	559.5 mW/m K
liquid at 100°C	678.6 mW/m K	644.4 mW/m K
vapor at 100°C	25.1 mW/m K	—
Adiabatic compressibility at 20°C	4.555 × 10 <sup>-12</sup> m <sup>2</sup> /N	4.70 × 10 <sup>-12</sup> m <sup>2</sup> /N
Dielectric relaxation time		
ice at -10°C	5 × 10 <sup>-5</sup> s	9.1 × 10 <sup>-5</sup> s
liquid at 25°C	9.22 × 10 <sup>-12</sup> s	11.89 × 10 <sup>-12</sup> s
Molecular magnetic susceptibility at 20°C	-12.972 × 10 <sup>-6</sup>	-12.948 × 10 <sup>-6</sup>
Surface tension of liquid water		
at 0°C	74.64 × 10 <sup>-3</sup> N/m	—
at 20°C	72.75 × 10 <sup>-3</sup> N/m	72.57 × 10 <sup>-3</sup> N/m
at 100°C	58.89 × 10 <sup>-3</sup> N/m	58.85 × 10 <sup>-3</sup> N/m
Refractive index at 20°C	1.333	1.328

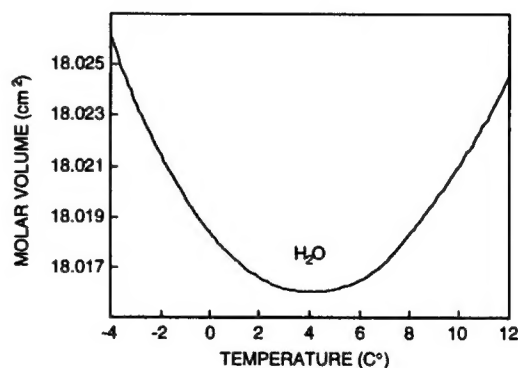
The chemical formula H<sub>2</sub>O doesn't exhaust the content of "absolutely" chemically pure water because of the presence of hydrogen and oxygen isotopes.

Three hydrogen isotopes are known: <sup>1</sup>H—ordinary hydrogen; <sup>2</sup>H or D, deuterium; and <sup>3</sup>H or T, tritium. In natural water there are 15 deuterium atoms per 10<sup>5</sup> hydrogen atoms. Tritium is β-radioactive. It disintegrates, electrons and neutrinos being emitted from the nucleus, and transforms into <sup>3</sup>He with a half-life of 12.43 years. Minute amounts of tritium water, T<sub>2</sub>O (melting temperature 4.5°C), can be either synthesized or found in small quantities near some radioactive sources, while so-called heavy water (mainly in the form of D<sub>2</sub>O) is an integral part (although a small one, 0.015%) of the world. At present it is widely used in various industries and scientific research.

There are also six known oxygen isotopes: <sup>14</sup>O, <sup>15</sup>O, <sup>16</sup>O, <sup>17</sup>O, <sup>18</sup>O and <sup>19</sup>O. Among them, only three are stable: <sup>16</sup>O, <sup>17</sup>O and <sup>18</sup>O. For every 10<sup>4</sup> atoms of <sup>16</sup>O, there are 20 atoms of <sup>18</sup>O and 4 atoms of <sup>17</sup>O.

Some basic physical properties of ordinary (H<sub>2</sub>O) and heavy (D<sub>2</sub>O) water are summarized in Table 1 (Malenkov 1988).

One of the surprising and peculiar properties of water is the presence of a density maximum at 4°C (Fig. 1). Because of this maximum, water freezes from the surface rather than from bottom. It is hard to imagine what



**Figure 1. Temperature dependence of a molar volume of water in the region of the density maximum (after Malenkov 1988).**

ecological catastrophe might result if there were no such "minor" peculiarity of water. Despite the widely accepted opinion that such behavior is unique, similar peculiarities in the density of a liquid phase are found in the case of  $\text{In}_2\text{Te}_3$  (Stillinger 1990).

Analogous density maxima are observed in the case of  $\text{D}_2\text{O}$  at  $T = 11.2^\circ\text{C}$  and  $\text{T}_2\text{O}$  at  $T = 13.4^\circ\text{C}$  (Stillinger 1990).

Another unusual property of water—decrease of specific volume at melting (8.3%)—is also vital for ecological equilibrium. Because of this ice floats on the water surface. This property is not unique either; it is also observed in Ge, Si and Bi.

The structure of ordinary water will be considered in the *Position of Oxygen Atoms* section, along with the structure of ice, and a comparison analysis will be performed.

## THE WATER MOLECULE

One of my colleagues, an expert in physical chemistry, said once that he had spent 25 years studying the properties of the water molecule. He realized that his whole life was not enough to answer all the questions about this molecule, consisting of only three atoms. Taking into account his experience, we shall abide by considerations of reasonable sufficiency for the rest of the material.

We shall begin our acquaintance with the water molecule with a consideration of its external characteristics—its shape and dimensions. The main sources of the information discussed below are X-ray diffraction, optical and electron scattering spectra of water vapor, measurements of the heat capacity of water vapor and, finally, theoretical calculations.

The first thing that strikes and excites the imagination when one looks at a water molecule is its triangular shape. The arrangement of oxygen and hydrogen nuclei in this molecule is shown in Figure 2. At first glance, such a strange shape with low symmetry (compared to a linear atomic arrangement) is not justified; it violates the principles of simplicity and rationality that we admire so often in the world around us.

Fortunately, the schematic in Figure 2 doesn't reflect all the features of the  $\text{H}_2\text{O}$  molecule's structure, which are determined by the exterior contours of electron clouds of the molecule. As we shall see further, the shape of these electron clouds is symmetrical to a very large extent and is able to satisfy our unconscious aspiration to harmony.

The arrangement of atoms in the vertices of a triangle, represented in Figure 2, is not the only possibility. Alternative configurations of the  $\text{H}_2\text{O}$  molecule appear when the molecule is excited (for instance, by ultraviolet light) and when the molecule undergoes transition from the ground state (with minimal energy) to one of the excited states (Claydon et al. 1971).

Table 2 contains values of OH bond lengths and the angles between them, calculated for several energy states of the  $\text{H}_2\text{O}$  molecule. At this point we are not going to focus on the meaning of the chemical symbols denoting different states. For us it is only essential to know that the symbol representing the ground state, with which we shall mainly deal, is situated in the upper row of this table, and other states differ from the ground state by energies of several electronvolts. As can be seen

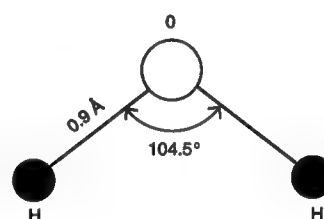


Figure 2. Arrangement of oxygen and hydrogen nuclei in water molecule.

Table 2. Equilibrium geometry of the lowest electronic states of  $\text{H}_2\text{O}$  with respect to symmetrical stretching and bending coordinates (after Claydon et al. 1971).

State	Valence MO configuration	Bond length (Å)	Bond angle (deg.)	Energy minimum (eV)	Vertical excitation energy (eV)
<b>Singlets</b>					
$X^1A_1$	$3a_1^21b_1^2$	1.03 <sub>0</sub>	104	0.00	—
$A^1B_1$	$3a_1^21b_14a_1$	1.11 <sub>5</sub>	180	5.79	7.43
$^1A_2$	$3a_1^21b_1^22b_2$	1.11 <sub>0</sub>	76	6.93	8.03
$B^1A_1$	$3a_11b_1^24a_1$	1.11 <sub>5</sub>	180	5.79	10.85
$^1B_2$	$3a_11b_1^22b_2$	1.10 <sub>0</sub>	122	10.27	11.06
<b>Triplets</b>					
$^3B_1$	$3a_1^21b_14a_1$	1.11 <sub>7</sub>	180	4.76	6.20
$^3A_2$	$3a_1^21b_12b_2$	1.11 <sub>7</sub>	80	6.55	7.49
$^3A_1$	$3a_11b_1^24a_1$	1.11 <sub>0</sub>	180	4.76	8.67
$^3B_2$	$3a_11b_1^22b_2$	1.11 <sub>5</sub>	112	8.90	9.43

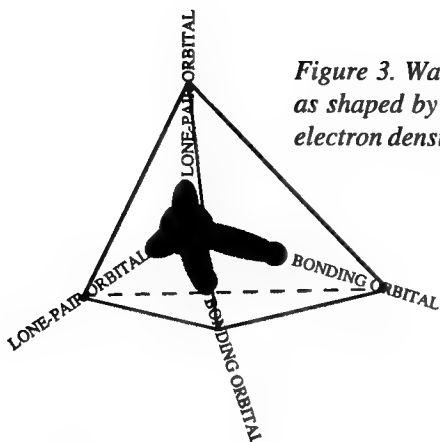


Figure 3. Water molecule as shaped by "clouds" of electron density.

from Table 2, among excited states there are states with a linear configuration (angle H-O-H is  $180^\circ$ ). To understand the factors that govern the shape of the molecule, one has to consider the configuration of electron clouds. Remember, the exact solution of Schrodinger's equation for such a complicated, many-body system, like the water molecule, doesn't exist. Several highly effective, computational, semi-empirical techniques have been developed that allow us to calculate with good accuracy the reciprocal arrangement of the oxygen and hydrogen nuclei and the electron density distribution, as well as energy levels in this molecule.

The electron cloud of the hydrogen atom consists of a single electron, occupying a spherically symmetrical 1s orbital. In the oxygen atom, two inner electrons are located at the 1s orbital, two at the 2s orbital (also spherically symmetrical), and the other four electrons at the external 2p orbitals. Electrons of these 2p orbitals are divided among three states (2p<sub>z</sub> has two electrons; 2p<sub>y</sub> and 2p<sub>x</sub> have one electron each).

According to modern concepts, when two hydrogen atoms with their electrons are attached to an oxygen atom, eight electrons take part in the formation of external molecular orbitals: two from the hydrogen and six from the 2s and 2p orbitals of oxygen. This process is thus called s-p hybridization. The water molecule electron cloud, consisting of four orbitals, each having two electrons, results from this hybridization (Fig. 3).

The exterior shape of the molecule, depicted in this figure, is determined by the electron density in the region around the oxygen and hydrogen nuclei. The molecule resembles a four-horned snail, the horns of which point approximately in the directions of the vertices of a regular tetrahedron. The H-O-H angle in the water molecule is equal to  $104.523^\circ$ , while the corresponding angle in a regular tetrahedron is  $109.467^\circ$ . The distance O-H in equilibrium is  $0.958 \text{ \AA}$ .

The two molecular orbitals in which the hydrogen nuclei are located are called "bonding orbitals," while the two others are called "lone-pair orbitals."

The electron density contour map for valence electrons in the plane H-O-H of a water molecule is shown in Figure 4 (Bader and Jones 1963).

The nature of the bond between oxygen and hydrogen in the water molecule is of particular interest. In the first place, since they share electrons, or "nationalize" them, one can say that this is covalent bonding. However, since a part of the electron cloud is "deferred" from the hydrogen atom to the oxygen atom, they assume opposite electric charges (+ at the hydrogen, - at the oxygen). The electrostatic attraction arising in this case is typical for ionic bonding. Therefore, one can talk about mixed ionic-covalent bonding in the case of the water molecule.

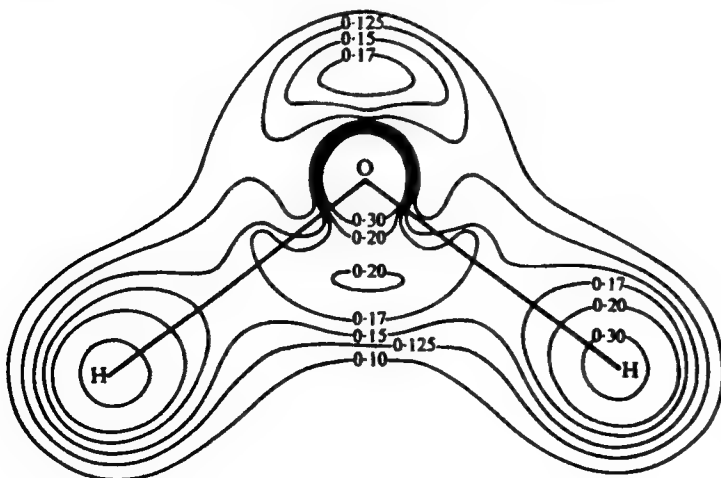


Figure 4. Electron density contours in the water molecule (after Bader and Jones 1963).

From our knowledge of electric charge distribution in the water molecule, the dipole moment can be calculated and compared to the value that can be derived from data on the dielectric permittivity of water vapor. Fairly good conformity exists between theoretical and experimental values

$$P_0 = (6.1 \pm 0.02) \times 10^{-30} \text{ C m.} \quad (2)$$

Owing to the presence of more than two point charges in a water molecule, it possesses multipole moments of higher orders than dipole: quadrupole and octupole. Though we are not going to employ these quantities, the reader can find detailed information about them in the paper by Glaeser and Coulson (1965), for instance. Let us also note that since the water molecule does not have an uncompensated magnetic moment in the ground state, it is diamagnetic (see Table 1).

Because of large bonding energies of hydrogen atoms and electrons in the water molecule, water is a very stable chemical compound. The energy of formation of the water molecule from an O and 2H atoms at 0 K is 9.51 eV. The energy required to remove a hydrogen atom from the oxygen atom is 5.11 eV for the first atom, and 4.40 eV for the second atom. Photodissociation of water molecules (in water vapor) begins at photon energies  $\geq 7.51$  eV ( $\lambda \leq 165$  nm).

At this point, we finish our short review of this important molecule. Properties of the  $\text{H}_2\text{O}$  molecule associated with rotations and oscillations will be considered in the report on the optical properties of ice.

## THE HYDROGEN BOND

The water molecule, described in the previous section, is the block that we shall use to build the crystal lattice of ice. As can be seen from Figure 3, the water molecule ideally fits the role of construction element for building an ice lattice. This molecule already has four "hands"—i.e., four molecular orbitals—stretched towards its neighbors. Two of those hands have a positive charge, owing to the presence of protons, and the other two have a negative charge. This allows the considerable electrostatic forces acting between molecules to be engaged when molecules associate to form a crystal. Each individual molecule forms bonds with four neighboring molecules, as is illustrated in Figure 5.

Two adjacent molecules appear to be connected via the hydrogen atom. This type of bond is usually denoted  $\text{O}-\text{H}\cdots\text{O}$  and is called a hydrogen bond. Other atoms, as well as oxygen, can form hydrogen bonds. Thus, the general symbol for the hydrogen bond is:  $\text{A}-\text{H}\cdots\text{B}$ . Atoms A and B must be electronegative and there must be a strong covalent bond between one of them and the hydrogen atom.

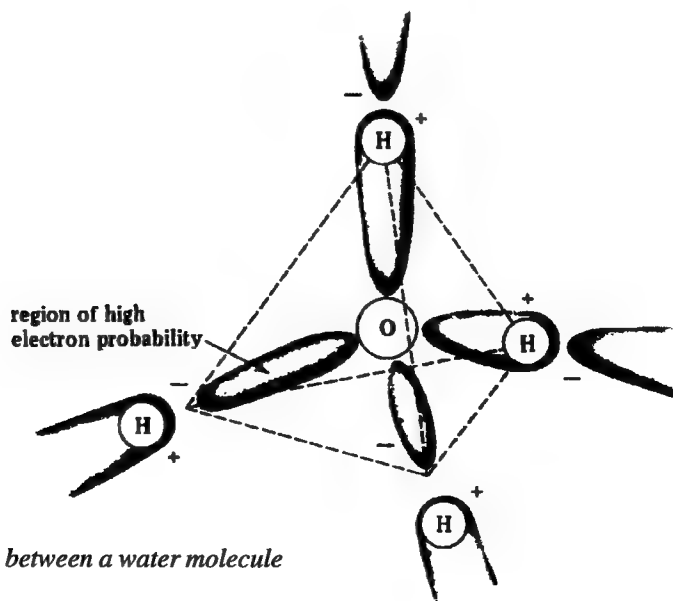


Figure 5. Formation of four hydrogen bonds between a water molecule and its four nearest neighbors.

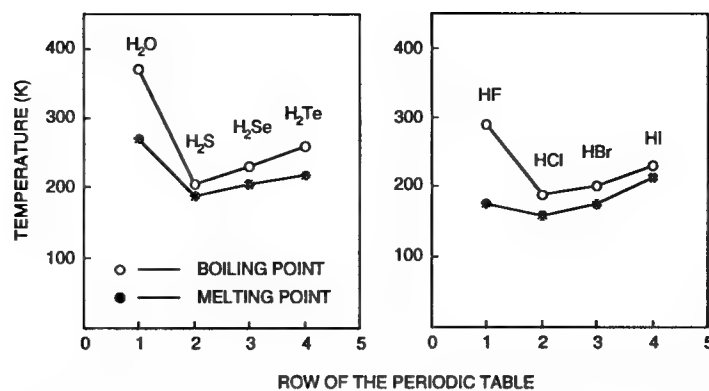


Figure 6. H-bond formation by  $\text{H}_2\text{O}$  and  $\text{HF}$  revealed by melting and boiling point trends.

To the very first approximation, hydrogen bonding arises from the electrostatic interaction between an electronegative atom and a proton. As a result, the distance between electronegative atoms becomes approximately equal to the sum of Van der Waals atomic radii; in other words, they act as if there were no hydrogen atom between them at all. For example, in the case of ice, the distance between two adjacent oxygen atoms  $r_{\text{oo}} = 2.76 \text{ \AA}$ , which is rather close to the sum of Van der Waals radii for oxygen:  $2 \times 1.4 \text{ \AA} = 2.8 \text{ \AA}$ .

The energy of the hydrogen bond is 1 to 1.5 orders of magnitude lower than the energy of a typical chemical (covalent) bond, but at the same time it is 2 to 3 orders of magnitude higher than the corresponding energy of non-valent Van der Waals interaction. An extremely strong hydrogen bond develops between  $\text{HF}$  molecules, which can associate to form polymer structures  $\text{H}_2\text{F}_2$ ,  $\text{H}_3\text{F}_3$ , ...,  $\text{H}_6\text{F}_6$ . Let us note also that a hydrogen bond can be not only intermolecular, but intramolecular as well. Such intramolecular bonds are one of the major factors stabilizing globular proteins. They also considerably affect the properties of wood and paper consisting of cellulose fibers, and are responsible for the unique structure of nucleic acids.

Because of the presence of a branched and rather dense net of hydrogen bonds, ice is a perfect model material for studying a variety of processes (proton transfer, for instance) that occur in more complex organic compounds.

As one of the parameters for characterizing the strength of hydrogen bonds between molecules, the values of melting temperature  $T_m$  and boiling temperature  $T_b$  can be taken. In Figure 6, values for  $T_m$  and  $T_b$  for hydrates of bivalent and monovalent compounds are plotted. As is clear from this figure, water possesses an exceptional position here, having the highest melting and boiling temperatures. In common ice ( $\text{I}_h$ ), the energy per hydrogen bond is 0.306 eV (Whalley 1957, 1976). This quantity is calculated as half the energy required to move a molecule from ice into the vapor (the half arises from the number of hydrogen bonds contributed by an individual water molecule to the overall structure).

## PHASE DIAGRAM OF WATER AND ICE

As mentioned previously, here we shall deal mainly with the structure of ordinary ice, denoted as  $\text{I}_h$ . The subscript  $h$  indicates that the structure has a hexagonal symmetry. Water is an extraordinary substance in many respects, including the number of solid phases—at present, 14 of them are known. Therefore, we will characterize the temperature and pressure ranges in which ice  $\text{I}_h$  exists, and the conditions under which other modifications of ice are found.

The phase diagram of ice in the pressure range 0 to 2.5 GPa and the temperature range  $-200$  to  $-100^\circ\text{C}$  is represented in Figure 7 (Whalley 1976). We shall give a detailed treatment of the structure and properties of high pressure phases in another report. Here, we shall only point out that all ice phases shown in Figure 7 are characterized by the water molecule retaining its individuality and yet being linked by hydrogen bonds to four neighbors. The closest (in terms of the structure) "relative" of ice  $\text{I}_h$  is cubic ice  $\text{I}_c$ . Cubic ice  $\text{I}_c$  can be obtained by water vapor sublimation onto a substrate in the temperature interval from  $-80$  to  $-150^\circ\text{C}$  (Honjo et al. 1956). Ice  $\text{I}_c$  can also be obtained when pressure is removed from some of the high pressure phases. Thus, Bertie et al. (1963) discovered that ice  $\text{I}_c$  can be produced in large quantities "by first preparing ices II, III or V at high pressures, cooling them to liquid nitrogen temperatures, reducing the pressure to atmospheric, and then warming."

Another crystallographic phase of ice, named ice IX, forms during the slow cooling of KOH-doped ice  $I_h$  below 72 K (Tajima et al. 1982). Finally, at enormous pressures  $P \geq 44$  GPa, so-called symmetrical ice (ice X) arises, in which protons occupy symmetrical positions with respect to the closest oxygen atoms. The relative positions of ices X (symmetrical-bond), VIII, VII, VI and the liquid phase are shown on the P-T diagram in Figure 8, adopted from a theoretical paper of Stillinger and Schweizer (1983). In fact, the division of individual molecules vanishes in ice X, because, owing to the symmetrical position of the hydrogen with respect to the oxygen, it is impossible to tell to which molecule a particular hydrogen atom belongs.

Among the 12 crystallographic forms of ice (ice  $I_c$ ,  $I_h$ , II, ..., XI), only 5 (II, VII–XI) are real crystals, in which a translational symmetry (the pattern is repeated when one goes from one unit cell to another) holds for both oxygen and hydrogen atoms. In other modifications of ice, the hydrogen subsystem is disordered. We shall consider this “disorder” in detail in the *Arrangement of Protons and Configurational Entropy of Ice* section.

The other two solid phases (which extend the sequence to 14) are amorphous forms of ice. The first one, low-density amorphous ice, can be produced when vapor is condensed onto a substrate at a temperature of about  $-150^\circ\text{C}$ . The density of this phase is  $0.94 \text{ Mg m}^{-3}$ . The second kind of amorphous ice, high-density amorphous ice, forms at  $T = 77 \text{ K}$  and pressure  $P \geq 1 \text{ GPa}$ . Its density (renormalized to a pressure of 1 atm) is  $1.17 \text{ Mg m}^{-3}$  (Whalley et al. 1987).

We also will be interested in the behavior of ice, water and water vapor in the vicinity of the so-called triple point ( $+0.01^\circ\text{C}$ , 610 Pa), at which all three phases exist in equilibrium. Figure 9, adapted from Maeno (1981), shows the phase diagram of water in the vicinity of this triple point and phase transformations.

## ARRANGEMENT OF OXYGEN ATOMS

I have no doubt that readers of this report have repeatedly noted the hexagonal shape of most snow crystals (Fig. 10). It is fairly easy to deduce that this shape arises from the symmetry of ordinary ice crystals at the molecular level. How does such hexagonal symmetry arise?

To understand this, let us consider a dense packing of identical, ideal balls on a level surface (Fig. 11).

After the first layer (let us denote it as A) and the second layer (B) are packed, there are two alternatives left for the third layer. First, the centers of the balls in this third layer can be either right above the centers of the balls in the first layer, i.e., in positions A, or, second, in positions C.

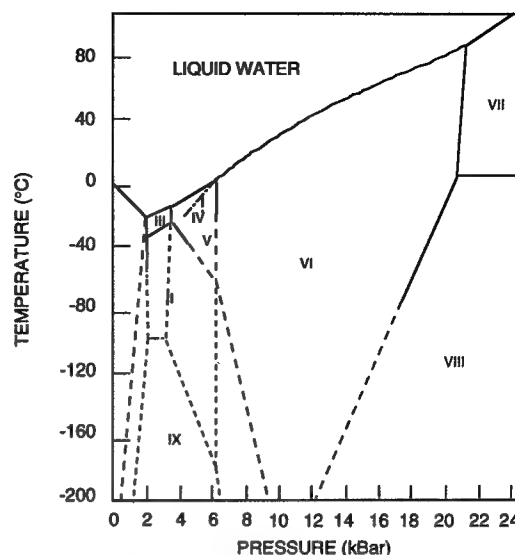


Figure 7. Phase diagram of ice in the pressure range 0 to 2.5 GPa (0 to 25 kBar) and the temperature range  $-200$  to  $-100^\circ\text{C}$  (after Whalley 1976).

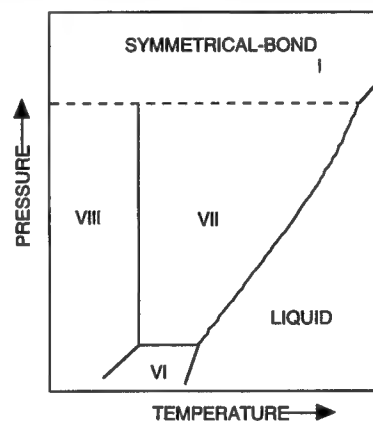


Figure 8. Very high-pressure region of the  $\text{H}_2\text{O}$  phase diagram (after Stillinger and Schweizer 1983).

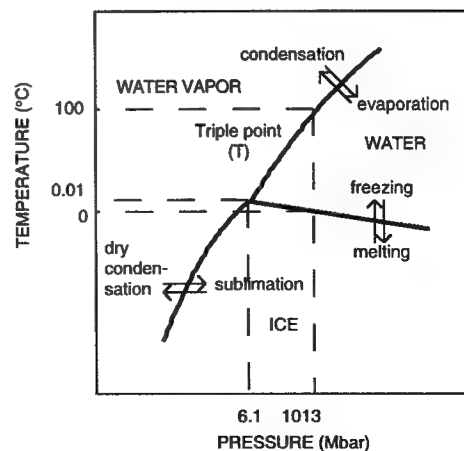


Figure 9. Low-pressure region of the  $\text{H}_2\text{O}$  phase diagram (after Maeno 1981).

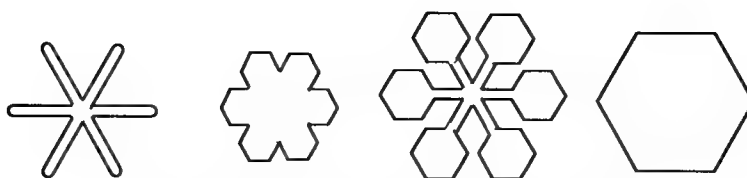


Figure 10. Hexagonal shape of snow flakes.

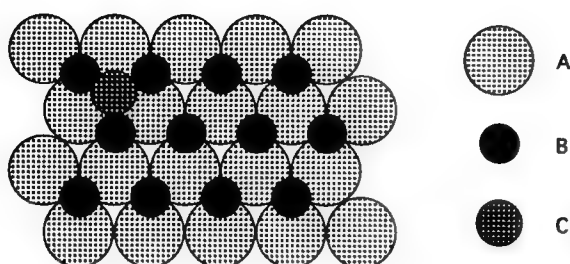


Figure 11. Dense packing of identical, ideal balls on a level surface.

If consecutive layers of balls are packed in the order ... ABABAB..., then the structure known as hexagonal close-packed will result. If we now replace the balls with dumbbells, consisting of two oxygen atoms connected by a hydrogen bond normal to the plane of the layers, then we obtain an almost exact arrangement of oxygen atoms in the lattice of ice  $I_h$ . Such a structure in two projections is shown in Figure 12.

The arrangement of oxygen atoms in the ice crystal lattice was derived from numerous data from X-ray diffraction. The major source of scattering of X-rays in a crystal is electrons. Therefore, the oxygen atom, surrounded by 10 electrons (eight of its own and two from hydrogen) is quite an efficient source of scattering, from which fairly good X-ray photographs may be obtained. The situation is quite unsatisfactory for the hydrogen atom, which is virtually "stripped" of its electrons. This is why the arrangement of hydrogen atoms in ice was inferred mainly from other sources—neutron diffraction and NMR.

When comparing the ice  $I_h$  structure to the structure of close-packed balls, one should take into account that the ice lattice is slightly squashed along the  $c$ -

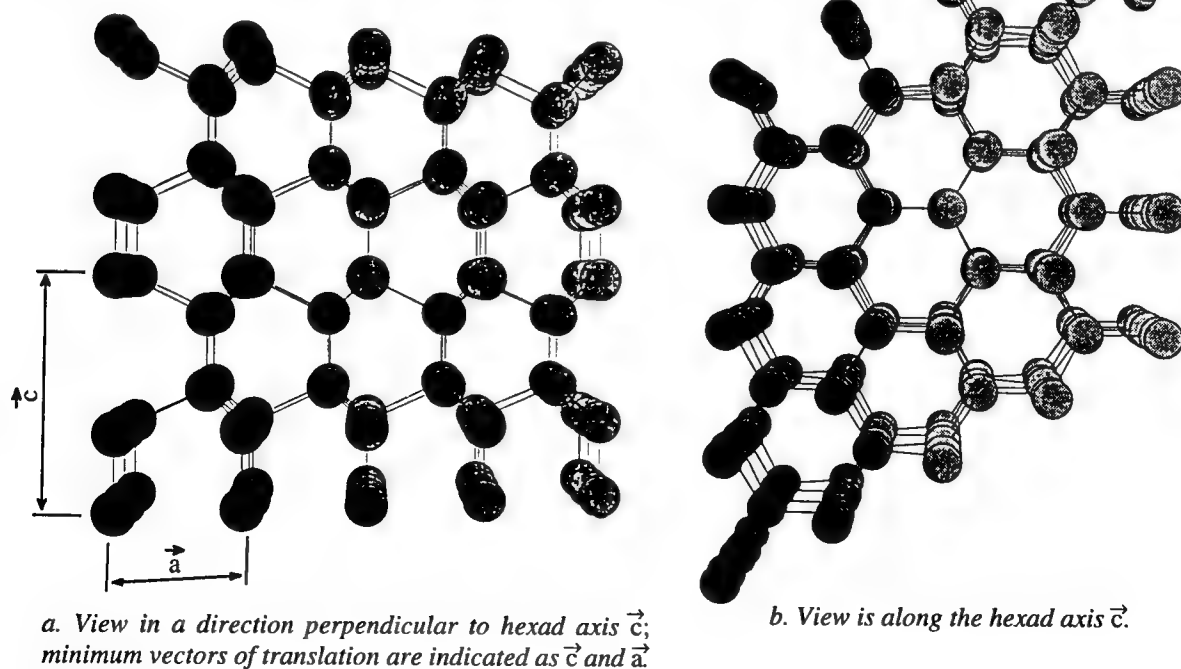


Figure 12. Positions of oxygen atoms in the ice  $I_h$  crystal. The shown size of atoms is not in real proportion to the inter atomic distance. Solid lines represent hydrogen bonds.



**Table 3. X-ray diffraction measurements of the unit-cell parameters of ice  $I_h$  as a function of temperature.**

Temperature (°C)	$a_0$ (Å)	$c_0$ (Å)	$c_0/a_0$	Temperature (°C)	$a_0$ (Å)	$c_0$ (Å)	$c_0/a_0$
From LaPlaca and Post (1960)				From Brill and Tippe (1967)			
-10	4.5190	7.3616	1.6291	-80	4.5108	7.3438	1.62804
-20	4.5169	7.3570	1.6288	-100	4.5062	7.3360	1.62798
-40	4.5128	7.3500	1.6287	-120	4.5025	7.3298	1.62794
-60	4.5088	7.3440	1.6289	-140	4.5000	7.3261	1.62802
-80	4.5052	7.3388	1.6290	-160	4.4987	7.3240	1.62803
-100	4.5021	7.3344	1.6291	-180	4.4979	7.3225	1.62798
-120	4.5001	7.3304	1.6289	-200	4.4974	7.3215	1.62794
-140	4.4990	7.3267	1.6285	-220	4.4971	7.3208	1.62789
-160	4.4961	7.3233	1.6288	-240	4.4969	7.3202	1.62783
-180	4.4948	7.3201	1.6286	-260	4.4968	7.3198	1.62778

axis. In the case of ice, the ratio  $c/a = 1.6293$  (Megaw 1934). In case of balls, the corresponding ratio is  $c/a = 2\sqrt{2}/\sqrt{3} = 1.633$ .

Owing to thermal expansion, parameters  $a$  and  $c$  (and their ratio) change with temperature (Table 3).

When “dumbbells” are packed according to the scheme ... ABCABCABC ... the structure of cubic ice  $I_c$  results, which is the closest “relative” of ice  $I_h$ .

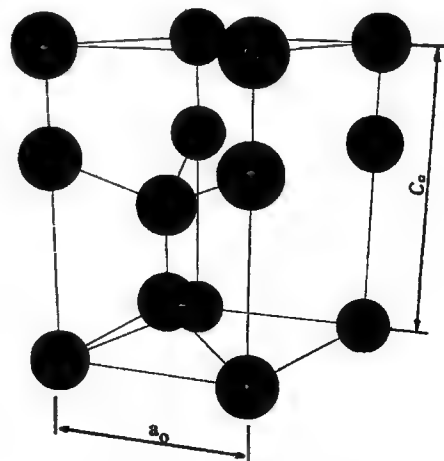
The symmetry of the crystal lattice, consisting of oxygen atoms, is characterized the space group  $P6_3/mmc$ . In this notation, “P” indicates that the space lattice is primitive, and “6<sub>3</sub>” means that the principal symmetry axis ( $c$ -axis) is a hexagonal screw axis. This implies that if an array of oxygen atoms is rotated and displaced simultaneously along that axis (in a screw-like motion), such that the displacement is  $c$  per revolution, then the first coincidence will occur when atoms are displaced along the  $c$ -axis by  $c/2$ . In other words, the symmetry of the  $c$ -axis is lower than six-fold. In the case of a pure rotation (without translational motion) about that axis by  $1/6$  of a full turn ( $360^\circ/6 = 60^\circ$ ), the coincidence of all atoms will not take place. Other symmetry elements in the point group indicate the presence of planes of symmetry (mirror,  $m$ ; and glide plane,  $c$ ). I refer readers who are interested in a detailed description of these elements of symmetry to one of the textbooks, Nye (1989) for instance. Let us look at cases when these elements of symmetry are somehow related to the symmetry of particular physical properties of ice.

The major component of the ice crystal lattice is a water molecule, surrounded by four neighboring molecules and linked to them by hydrogen bonds. At  $T = 0^\circ\text{C}$  the distance between the centers of the closest oxygen atoms  $r_{oo} = 2.76 \text{ Å}$ , and the angles between hydrogen bonds are very close to the angles between bisectors of a right tetrahedron  $-109^\circ 28'$ .

A unit cell of  $I_h$  structure is shown in Figure 13. The whole crystal can be built from unit cells by the consecutive process of attaching one cell to another.

Let us calculate the number of oxygen atoms per unit cell of  $I_h$  ice. We can see that eight atoms are located in the vertices of the tetrahedron, each thus belonging to eight unit cells simultaneously, and four atoms are on the edges, i.e., shared among four unit cells. Therefore, there are  $8/8 + 4/4 + 2 = 4$  oxygen atoms or water molecules per unit cell.

The coordinate system defining the positions of all oxygen atoms as well as crystallographic planes is formed by lattice vectors coinciding with the edges of the unit cell. When characterizing a hexagonal lattice, it is more convenient to use four rather than three unit vectors, as is illustrated in Figure 14. Three of these vectors lie in the plane perpendicular to the hexagonal  $c$ -axis, and the fourth vector coincides with the  $c$ -axis. Examples of coordi-



**Figure 13. Unit cell of ice  $I_h$ .**

nates of some points in this basis are shown in the same figure. In the Miller-Bravais system, the potential redundancy caused by having three coplanar lattice vectors is resolved by ensuring that the first three coordinates sum to zero.

The advantage of a four-index system of notation is that all physically equivalent points (in the case of hexagonal symmetry) can be obtained by rearranging the first three indices. For instance, all the vertices of a hexagon have coordinates of the type  $1/3[1120]$ , for example,  $1/3[2110]$ ,  $1/3[1210]$  and so on.

If for  $(hki\bar{l})$  plane either  $l = 0$  or  $h, k, i$  all  $= 0$ , then the plane is perpendicular to  $[hki\bar{l}]$  vector. Thus,  $(0001)$  denotes the plane normal to the  $c$ -axis. This plane is called the basal plane and is the plane of the closest packing in  $I_h$  structure. Other close-packed planes are prismatic planes, parallel to the  $c$ -axis. There are prismatic planes of the first order  $(1100)$  and of the second order  $(1120)$ . Planes that form an angle with the  $c$ -axis ( $\neq 0^\circ$  and  $\neq 90^\circ$ ) are called pyramidal.

In conclusion, let us briefly consider the similarities and differences between the structures of ice  $I_h$  and water. Specifically, we shall try to understand why the density of water is higher than that of ice.

Experimental and theoretical studies of water structure carried out in the 1970s and 1980s revealed a certain random, tetrahedral network of hydrogen bonds in the liquid phase (Malenkov 1988). The average distance between adjacent water molecules is almost the same as in the case of ice, but the average number of closest neighbors is larger. In water this number is approximately 4.4, compared to 4 in ice  $I_h$ . This dissimilarity results in a larger density of water in comparison with ice.

There is a widely spread opinion that the lower density of ice is attributable to the "openness" of its structure, in which there appear to exist a lot of "voids." Figure 15, in which the dimensions of atoms are given in the same scale as interatomic distances, appears to support this contention.

## ARRANGEMENT OF PROTONS AND CONFIGURATIONAL ENTROPY OF ICE

The crystal lattice consisting of oxygen atoms considered in the previous section does not exhaust by any means the description of the ice structure. We now have to find possible positions for an enormous number of protons in this lattice. This question is not trivial.

Even taking into account, from the comparison of optical spectra of water vapor and ice, that water molecules retain their properties and individuality in the ice lattice, there is still a huge number of possible distributions of protons at hydrogen bonds in ice. We shall try to exemplify this. Let us consider an ice crystal consisting of  $N$  water molecules. Since the number of hydrogen bonds in the crystal is just the number of hydrogen atoms, then there are  $2N$  hydrogen bonds in this crystal. The proton on each bond "must know its master," i.e., it must be located closer to either one oxygen atom or the other.\*

\* If a proton were positioned in the middle of a hydrogen bond, it would result in a typical ionic crystal with a much higher melting point than ice (hundreds of degrees celsius), huge electroconductivity of the liquid phase (water) and much smaller dielectric permittivity  $\epsilon \approx 10$ , whereas in the case of ice  $\epsilon \approx 100$ .

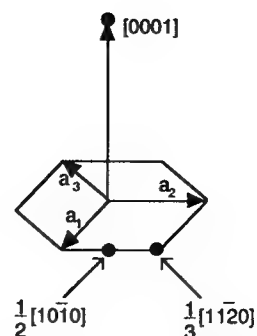


Figure 14. Coordinate system for hexagonal lattices.

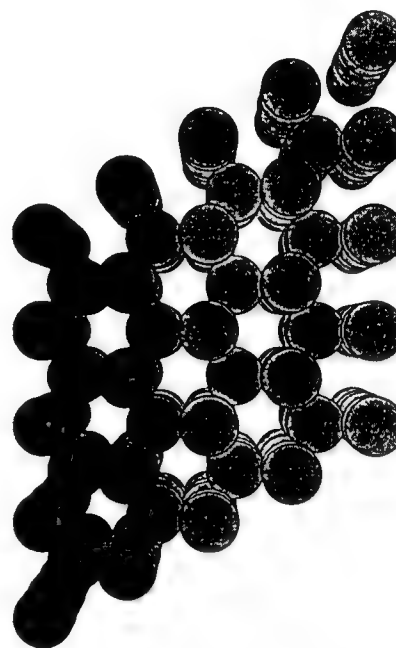


Figure 15. Same view of the ice  $I_h$  lattice as in Figure 12b, but with oxygen atoms represented by balls of Van der Waals radii.

Thus, we might expect  $(2)^{2N}$  possible arrangements of protons. This, of course, is an overestimated value, since there will be many incorrect molecules that have four, three, one or zero protons instead of two. Still, it is clear that the number of remaining configurations is enormous.

We can also approach the problem from the other end, focusing our attention on a water molecule. If we specify the positions of its four nearest neighbors in space, i.e., four hydrogen bonds, there are still six possible orientations of the molecule left, as shown in Figure 16. Since the total number of molecules is  $N$ , then in the case of their independent arrangement, we might expect  $(6)^N$  various combinations, which will actually differ from each other only by proton arrangement. But this value is again overestimated, since we are neglecting the order in hydrogen bonds, and among them there would be wrong bonds with two protons and without protons at all.

In our preceding simple discussion, two very significant principles that an "ideal" or defectless ice structure must obey have been employed:

1. There are two protons near each oxygen atom.
2. There is a single proton on a hydrogen bond.

The first principle states the electroneutrality of a water molecule in the ice crystal lattice, and the second one takes care of fulfilling the main principle of a hydrogen bond, the presence of a (single) proton at it.

Both principles were first introduced by Bernal and Fowler (1933), whose names they bear, and later were more seriously grounded and considered by Pauling (1935). Sometimes, these principles are just referred to as the "ice rules."

L. Pauling, twice a Nobel Prize winner, was the first to calculate with good accuracy the number of possible configurations of protons that satisfies the ice rules. His arguments were simple and elegant, and we will reproduce them.

As we mentioned above, it seems at first glance that we can distribute  $2N$  protons on  $2N$  hydrogen bonds in  $(2)^{2N}$  ways, given that there are two possible positions for a hydrogen atom on each bond.

However, if we consider four bonds attached to an oxygen atom (Fig. 16), then we see that, instead of the expected  $2^4 = 16$  configurations, only 6 are allowed. This means that for each lattice node a "reduction coefficient" of  $6/16$  must be used, which becomes  $(6/16)^N$  in the case of  $N$  nodes. Then, the total number of configurations  $W$  will be given by

$$W = (2)^{2N} \times (6/16)^N = (3/2)^N. \quad (3)$$

The value of  $W$  is still not absolutely exact for two reasons. The first is that water molecules in the structure of ice  $I_h$  are incorporated in closed rings, the smallest of which comprises six molecules (see Fig. 12b, for instance). Therefore, reorientation of a single molecule in the ring causes reorientation of others, if the ice rules are not to be violated. This circumstance is extremely difficult to take into account. The closest approximation was reported by Nagle (1966) who found

$$W = (1.50685 \pm 0.00015)^N. \quad (4)$$

This deviates by less than 0.5% from the crude result (eq 3) of Pauling!

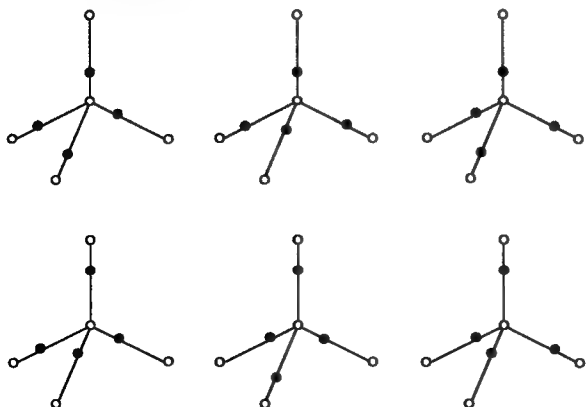


Figure 16. Six possible orientations of the water molecule in the ice  $I_h$  lattice.

Another circumstance not taken into account by Pauling was the fact that real ice has surfaces. The expression for  $W$  of a real ice crystal, of finite dimensions and with surfaces, was derived by Suzuki (1966). Since the ratio of molecules at the surface to molecules in the bulk tends to decrease rapidly with increasing volume, in most practical situations we can neglect this correction to  $W$ .

The above analysis implies that all allowed configurations have the same energy or that the energy difference is small in comparison with  $k_B T$ . And the experimental results support this hypothesis. But why are the Bernal-Fowler configurations almost isoenergetic? We don't know this yet.

We have considered the question of various configurations of the ice protonic subsystem and their number with this degree of thoroughness because we now have a chance to compare the predictions of this hypothesis with various experimental data.

First, if ice really has a disordered protonic subsystem, then there must be a quite large entropy associated with this disorder, which should manifest itself in the thermal properties of ice. Such entropy we will refer to as configurational entropy  $S_c$ . Another term sometimes used for this quantity is zero-point entropy.

The quantity  $S_c$ , according to the definition of entropy, is

$$S_c = k_B \ln W \quad (5)$$

where  $k_B$  is Boltzman's constant.

If one assumes that protonic disorder is preserved in ice at the lowest temperatures as well, then  $S_c$  can be found from the calorimetric measurements of heat  $Q$  that is liberated during the cooling of a certain amount of dilute water vapor (diluteness is necessary for the gas to be considered as an ideal gas). The change in the entropy of the system is

$$dS = \delta Q/T \quad (6)$$

and

$$\Delta S = \int_{T_1}^{T_2} \delta Q/T . \quad (7)$$

Starting an experiment with water vapor, one must follow its consecutive phases of condensation into the water phase and crystallization, measuring the heat released during phase transitions and that released because of heat capacity. Therefore, we start with the known value of  $S$  and track its behavior down to temperatures close to absolute zero. According to the third law of thermodynamics

$$\lim_{T \rightarrow 0} S = 0 \quad (8)$$

i.e., one might expect that the quantity determined in the experiment described above goes to zero. Such measurements have been performed several times on ice (see, e.g., Giauque and Stout 1936, Flubacher et al. 1960, Sugisaki et al. 1968).

Those measurements, instead of zero as expected from formula 8, yielded

$$\lim_{T \rightarrow 0} S = 3.41 \text{ J mol}^{-1} \text{ deg}^{-1} \quad (9)$$

which is remarkably close to the value predicted from formulas 4 and 5

$$S_c = k_B \ln W = (3.41 \pm 0.0008) \text{ J mol}^{-1} \text{ deg}^{-1} . \quad (10)$$

What does this result mean? That ice violates the third law of thermodynamics? That this law is not valid? Of course not. This confirms that a disorder in the protonic subsystem, and the configurational entropy associated

with it, exists! As we shall see in the report concerned with other forms of ice, the configurational entropy (or a disorder in the protonic subsystem) merely does not have enough time to vanish during the cooling of ice for purely kinetic reasons. The reorientation time of a water molecule in pure ice has already become much longer than a human's lifetime at liquid nitrogen temperature (77 K). However, if ice is slightly doped with KOH, which accelerates the process of molecular reorientation at low temperatures, then a transition occurs at a temperature of about 72 K to a partially ordered ice XI, which liberates most of the entropy (see, e.g., Tajima et al. 1982). What else might one expect to discover in an experiment, if such a disordered or "statistical" structure of the protonic subsystem exists?

According to the model described above, as introduced by Pauling and which is usually termed a statistical model, a proton can assume one of two positions on a hydrogen bond, and a proton switches from one position to the other many times per second. Since the orientation of the electric dipole moment of a water molecule is changed because of this, information about the reorientation time of water molecules may be provided by measurements of the dielectric permittivity of ice as a function of the frequency of the external electric field. If the characteristic time that it takes for the molecules to reorient is  $\tau$ , then, in the frequency range  $\omega \approx 1/\tau$ , the magnitude of the dielectric permittivity  $\epsilon$  must change markedly. This, in fact, is found to be the case in experiments, and for pure ice  $I_h$  at  $T = -10^\circ\text{C}$  the value of  $\tau \approx 5 \times 10^{-5}$  seconds was obtained. To film the positions of protons, we would need a high speed camera, operating at an amazing speed. When determining proton positions, if experimental techniques are used that require more time than  $\tau$  for the acquisition of the information (electron or neutron diffraction, for instance), the position of protons is averaged and at each point (of two) on a hydrogen bond we find a "half-proton."

Such measurements conducted by several research teams yielded exactly the same result. It was Peterson and Levy (1957) who were the first to apply neutron diffraction to determine the positions of hydrogen nuclei in monocrystals of ice  $I_h$ . Since, as a result of the interaction of the magnetic moment of a neutron with the randomly oriented magnetic momentum of a proton, a rather strong scattering occurs, Peterson and Levy conducted their

experiments on  $\text{D}_2\text{O}$  rather than on ordinary ice. (The magnetic moments of the proton and the neutron compensate each other to a large degree in deuterium nuclei.)

An arrangement of oxygen and hydrogen nuclei in an ice lattice is shown in Figure 17. It is important to note that O-H and H-H distances in ordinary and heavy ice can be slightly different. This distinction is determined by the amplitudes of both thermal and "zero-point" oscillations differing because of differences in the mass of H and D. Owing to the anharmonicity of the oscillations, the position of the center of mass depends on the amplitude and appears to be different for hydrogen and deuterium.

Extremely accurate measurements of proton positions in the ice  $I_h$  lattice were made by Kuhs and Lehmann (1981, 1983, 1987), who used neutrons with a small wavelength  $\lambda = 0.7107 \text{ \AA}$ . Distances O-O, O-H and H-H for three different temperatures are summarized in Table 4. Another interesting result is that the magnitudes of proton oscillations were determined (see Table 4). Owing to the proton having the smallest mass among all atomic nuclei, the magnitude of the oscillations turns out to be very significant, even at very low temperatures. Therefore, protons can be viewed as being "spread" or "distributed" over a region with dimensions of about  $0.5 \text{ \AA}$ , as is illustrated in Figure 18.

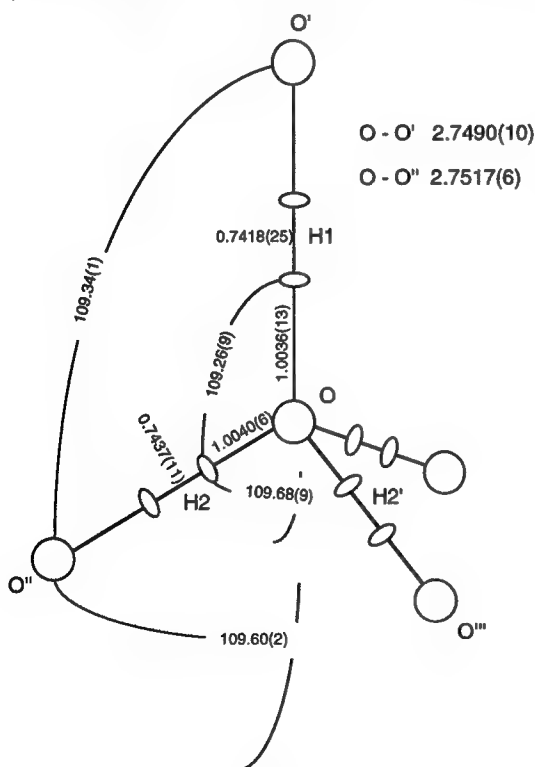
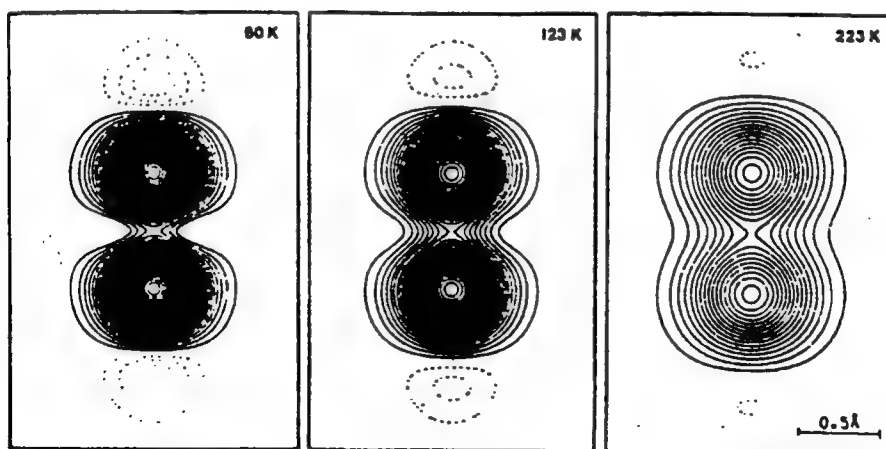


Figure 17. "Half-proton" picture for representing the proton arrangement in the ice  $I_h$  structure (after Peterson and Levy 1957).

**Table 4. Molecular geometry and thermal motion of ice I<sub>h</sub>.** The bonds O-H<sub>1</sub> and O-O' are along the crystallographic  $\vec{c}$  axis. Thermal motion is indicated as root-mean-square displacement (rmsd) in certain directions along or orthogonal to axis *a*, *c* or O-O'' (after Kuhs and Lehmann 1983).

	60 K		123 K		233 K	
Distances (Å)						
O-O'	2.750	(1)	2.751	(1)	2.759	(2)
O-O''	2.752	(1)	2.753	(1)	2.760	(1)
O-H1	1.004	(2)	1.008	(2)	1.008	(4)
O-H2	1.005	(1)	1.004	(1)	1.004	(2)
H1-H1'	0.741	(3)	0.735	(4)	0.744	(7)
H2-H2'	0.741	(1)	0.745	(2)	0.753	(3)
Angles (deg.)						
O'-O-O''	109.33	(2)	109.34	(2)	109.35	(4)
O'-O-O''	109.61	(2)	109.60	(3)	109.60	(5)
H1-O-H2	109.21	(11)	109.40	(16)	109.44	(27)
H2-O-H2'	109.73	(11)	109.54	(16)	109.50	(27)
Rmsd (Å)						
O $\parallel$ c	0.1179	(5)	0.1521	(7)	0.2069	(14)
O $\perp$ c	0.1183	(9)	0.1534	(8)	0.2096	(10)
H1 $\parallel$ a	0.1337	(16)	0.1626	(21)	0.2115	(41)
H1 $\perp$ c	0.1784	(6)	0.1988	(11)	0.2409	(28)
H1 $\parallel$ O-O''	0.1358	(10)	0.1650	(15)	0.2109	(31)
H2 $\parallel$ a	0.1799	(10)	0.2005	(14)	0.2421	(23)
H2 $\perp$ a	0.1762	(10)	0.1984	(15)	0.2407	(27)

Employing the data on the distribution of proton density along a hydrogen bond, Kuhs and Lehmann estimated the height of the potential barrier separating the two stable positions of a proton on a bond. They obtained for the height of the barrier the very small value of 0.012 eV, which can be easily surmounted by a proton, even at  $T = 0$  K, due to quantum tunneling. However, one must keep in mind that a proton cannot make such a transition from one well to another alone, because the first ice rule would be violated. Two charged ions would appear, which would have an energy of about 1 eV, much larger than the 0.012-eV barrier height. Only simultaneous



*Figure 18. Probability density map of H1 in the (10 $\bar{1}$ 0) plane as described by harmonic and anharmonic terms up to fourth order (equidistant contours, zero contour omitted). The small negative regions are due to minor shortcomings of the chosen mathematical description. With the limits of error, these probability densities are following the expectations for simple temperature dependence assuming Boltzmann statistics (after Kuhs and Lehmann 1983).*

(correlated) motion of protons along closed trajectories at hydrogen bonds is allowed by the ice rules without the formation of ions. An example of such a motion along the shortest ring, consisting of six water molecules, is shown in Figure 19. The question of the possibility of collective correlated motion of protons in ice is still a matter of controversy. We will return to it in the report concerned with point defects and solitons.

Shimaoka (1960) determined proton positions in ice using electron diffraction. Those experiments, which had much lower accuracy than the neutron diffraction technique, yielded the value of  $0.96 \pm 0.03 \text{ \AA}$  for the O-H distance.

Finally, Kuhs and Lehmann (1987), studying neutron diffraction in ice at very low (15 K) temperature, showed that, because of the "disorder" in the protonic subsystem, the oxygen lattice is also disordered. Namely, the exact positions of oxygen atoms deviate randomly (depending upon the node) from the corresponding positions in the ideal lattice by approximately  $0.01 \text{ \AA}$ .

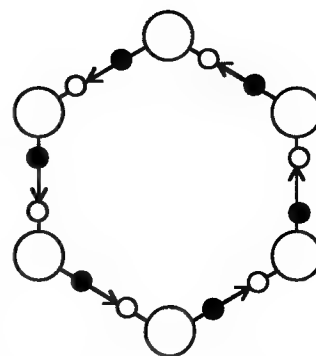


Figure 19. Correlated hops of six protons along the hydrogen bonds.

### SPATIAL NETWORK OF ELECTRONIC DENSITY OF ICE AND STRUCTURE OF ENERGY BANDS

One can say that ice is composed of the atomic nuclei of oxygen atoms and hydrogen atoms—protons and electrons. Now we have to consider the distribution of the latter in the ice structure.

From a methodological point of view, there are two quite different approaches to studying the electronic structure of ice. The first one is based on the use of certain techniques (X-ray diffraction, for instance) that directly respond to the magnitude of the electron density, thereby allowing us to reconstruct the spatial distribution of electrons in the ice crystalline structure.

In recent years, very significant results have been achieved in this area, owing to both advances in the design of X-ray devices and improvement of techniques for analysis of data (Goto et al. 1990, Sakata et al. 1991, 1992). The distribution of the electronic density in the three crystallographic planes of hexagonal ice is shown in Figure 20, adapted from the paper of Sakata et al. (1991), who used for the accurate structure analysis the Maximum Entropy Method (MEM).

Let us note, in the first place, that ice is permeated by a rather dense, three-dimensional network of electrons. This network "glues" individual water molecules into a rigid crystalline lattice, which is quite distinct from the concept of ice as a molecular crystal in which individual molecules interact very weakly.

Information about the distribution of electron density, such as that represented in Figure 20, is extremely valuable and can be employed to derive numerous properties and parameters of the material. In fact, since we already know the arrangement of oxygen and hydrogen atoms, we know the complete distribution of electric charges inside the ice lattice. This, in principle, allows us to calculate the energies of hydrogen bonds, the structure of filled electronic energy bands, elastic constants, etc. However, I am not aware of computations of this kind, which are based upon the data on the spatial distribution of the electron density, being carried out for ice.

Nevertheless, we can illustrate the relationship between the distribution of electrons in space and their energy characteristics while avoiding the use of sophisticated theoretical methods. In quantum mechanics there is a relationship between electron density and the minimal kinetic energy of electrons. If the motion of an electron along the  $x$ -axis is restricted to  $\Delta x$ , then the uncertainty in its momentum  $\Delta p_x$ , according to Heisenberg's uncertainty principle, cannot be less than

$$\Delta p_x \geq h/\Delta x \quad (10)$$

where  $h$  is Planck's constant. The corresponding uncertainty in the kinetic energy is

$$\Delta T = (\Delta p_x)^2/2m_e \geq h^2/2m_e (\Delta x)^2 \quad (11)$$

where  $m_e$  is an electron mass.

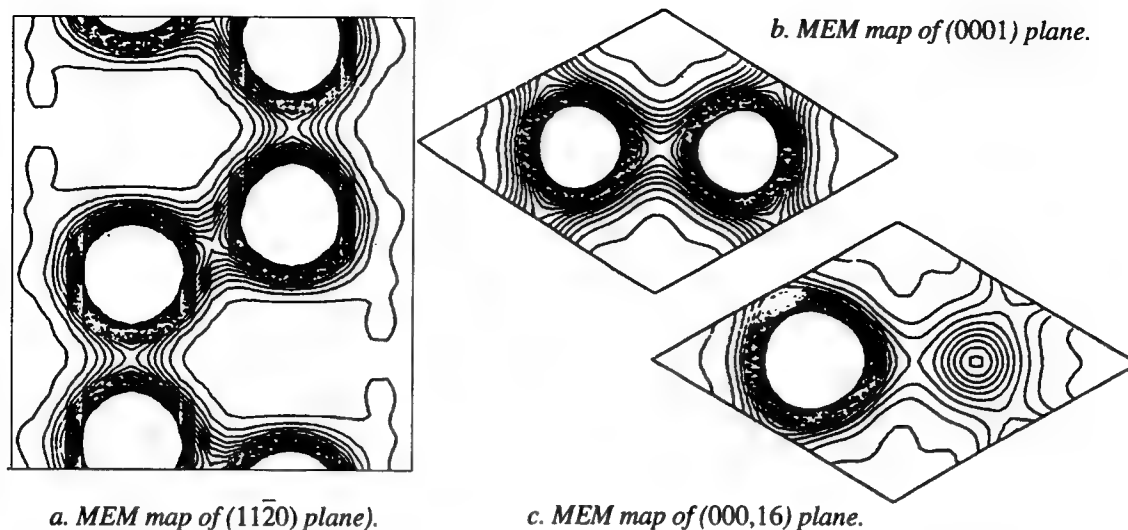


Figure 20. Electron density distribution of ice  $I_h$ . The density contours from 0 to  $1 \text{ \AA}^{-3}$  are shown (after Sakata et al. 1991).

In the case of motion that is restricted in three dimensions to a cube with side  $\Delta x$ , the uncertainty in the energy is three times greater

$$\Delta T = \Delta T_x + \Delta T_y + \Delta T_z \geq 3h^2/2m_e(\Delta x)^2. \quad (12)$$

Formula 12 can be rewritten, using the spatial density of electrons  $n = (\Delta x)^{-3}$

$$\Delta T \geq 3h^2/2m_e n^{2/3}. \quad (13)$$

The width of an individual electronic energy band in a solid is determined, to a first approximation, in terms of the difference between the maximum and minimum kinetic energy. Therefore, the result of formula 13 can be interpreted as a relationship between the local density of electrons  $n$  and the width of the energy band (or bands) to which the electrons belong.

The minimum density of the electrons at the lines of hydrogen bonds (Fig. 20) appears to be  $n = 3 \times 10^{23} \text{ cm}^{-3}$ , from which

$$\Delta T \geq 3h^2/2m_e n^{2/3} = 4.6 \text{ eV}. \quad (14)$$

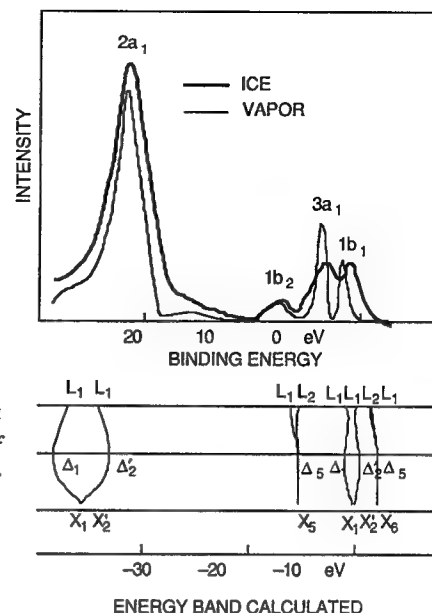
Such consideration may have sense only if the electron density  $n$  fills the whole crystal, so that we can use free electron gas model for the estimate.

The derived value (eq 14) should be regarded as only an order of magnitude, since we have used the mass of a free electron (in a vacuum)  $m_e = 9.109 \times 10^{-28} \text{ g}$ , and generally one should use the effective mass of the electrons in a given energy band. In experimental work by Shibagushi et al. (1977), the total width of the first three filled bands appears to be equal to about 2 eV and the maximum difference in the energies for the electrons in those bands is about 6 eV. Therefore, the crude estimate of formula 14 turns out to be midway between these two values. Is it large or small? It is well known that in isolated stable atoms and molecules electrons occupy discrete energy levels of zero width. As  $N$  molecules are brought together, each of these levels becomes split into  $N$  closely spaced levels, thereby forming an energy band. When bands are formed with an energy width of several atomic energies (about 10 eV), we obviously can no longer speak about isolated molecules and molecular spectra. Consequently, from the standpoint of the electronic structure, ice is more correctly considered a rather typical crystal with common electrons that can move about in three dimensions.

The second methodological approach for studies of the electronic structure of crystals is based on the use of experimental methods that are capable of determining the energy characteristics of electrons: the position of the bottom and top of electronic bands with respect to vacuum level, the band width, the position of the Fermi level



Figure 21. X-ray photoelectron spectra of ice. Light curve shows data of water vapor. The lower figure shows the electronic band structure of cubic ice calculated by Pastori-Parravicini and Resca (1973) (after Shibaguchi et al. 1977).



(the chemical potential of an electron in a crystal), the width of a forbidden band, etc. I shall list such experimental techniques below, along with examples of work in which those techniques have been employed for ice.

The first two methods—X-ray photoelectron spectroscopy and ultraviolet photoelectron spectroscopy—make use of the external photo effect. In these methods a beam of photons with energies greater than the binding energy of electrons in the material under investigation is absorbed by electrons in the crystal. A certain fraction of these electrons, located close to the surface, is knocked out into a vacuum and their kinetic energy is measured. Obviously, since the energy of the incident electrons is fixed, the kinetic energy of the electrons “knocked out” will decrease with increasing depth of energy. Thus, the kinetic energy spectrum of photoelectrons contains information about how deep the electron energy bands are and what their density of states is.

An example of an X-ray photoelectron spectrum of ice, in which at least four peaks are clearly seen that correspond to the four most shallow bands filled with electrons, is represented in Figure 21. In the same figure the spectrum of water vapor and the results of theoretical calculations of Pastori-Parravicini and Resca (1973) are shown for comparison. The nomenclature used in the theoretical diagram will be explained later in this section. An excellent example of ultraviolet photoelectron spectra is represented in Figure 22.

Another efficient source of information about the structure of the electron energy bands of ice is the spectrum of optical absorption in the range of vacuum ultraviolet. An example of such a spectrum is shown in Figure 23.

Shibaguchi et al. (1977) employed all three methods char-

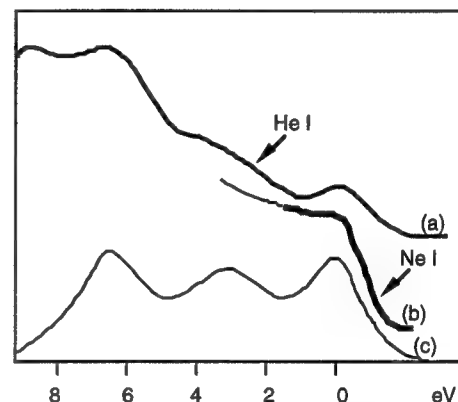


Figure 22. Photoelectron energy distribution curve of ice for (a)  $h\nu = 21.2$  eV and (b)  $h\nu = 16.8$  eV; (c) spectrum of ice obtained from curve (a) after subtraction of the background (after Abbati et al. 1979).

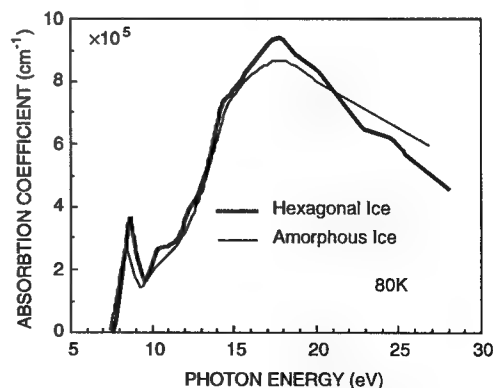


Figure 23. Absorption spectra of hexagonal ice and amorphous ice at 80 K (after Seki et al. 1981).

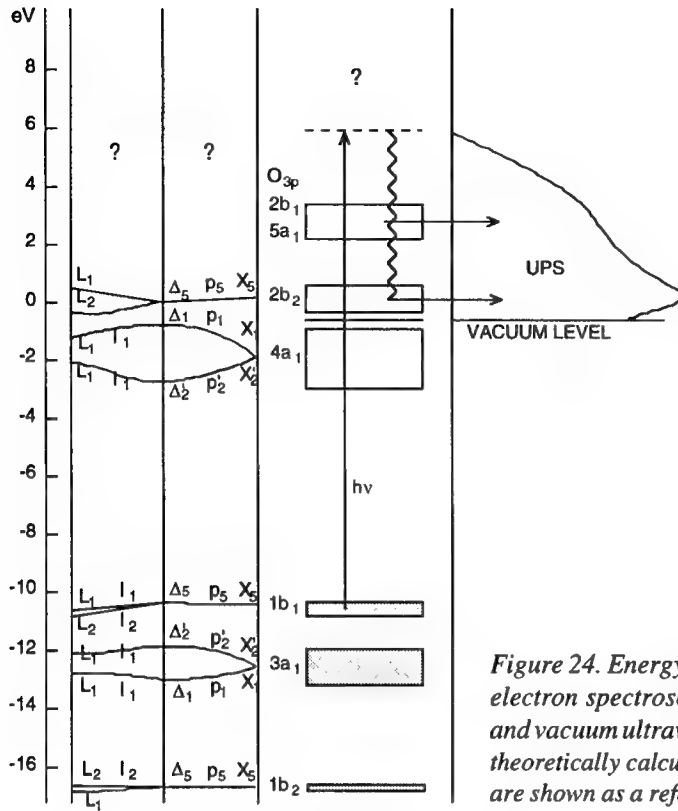


Figure 24. Energy level scheme of ice revealed by X-ray photoelectron spectroscopy, ultraviolet photoelectron spectroscopy and vacuum ultraviolet absorption spectra. The electronic bands theoretically calculated by Pastori-Parravicini and Resca (1973) are shown as a reference (after Shibaguchi et al. 1977).

acterized above to establish the positions of energy bands of ice. The results of their analysis are shown in Figure 24, in which the positions of energy bands are given relative to the energy of a free electron in a vacuum (denoted as vacuum level). According to this schematic, the width of the forbidden band of ice is  $E_G \approx 7.8$  eV. This is the distance between the top of the upper, filled band and the bottom of the lower, empty band.

Since the upper, filled band has no vacant states and the width of the forbidden band is huge compared to the thermal energy  $k_B T \approx 0.022$  eV ( $T = -10^\circ\text{C}$ ), from the point of view of electronic conductivity, ice must be an ideal dielectric. An estimate of the concentration of intrinsic electrons yields  $n \leq 10^{-133} \text{ cm}^{-3}$  at  $T = -10^\circ\text{C}$ . This means that in the whole Antarctic ice cap there is not a single electron that could conduct current and that would appear to be due to a thermoactivated transition from the valence band to the conductivity band.

At present, there are only a few works concerned with theoretical calculations of the energy bands of ice. The difficulties of such calculations arise because one cannot employ the powerful methods of solid state physics based on the use of symmetry elements. However, the structure of ice lacks even a translational symmetry. Therefore, the first calculations of the electron structure of ice by Pastori-Parravichini and Resca (1971, 1973) were performed on completely polarized ice (which has a maximum electrical dipole moment). In addition, cubic ice possessing higher symmetry than hexagonal ice has been considered in their calculations.

Before we proceed to a discussion of their results, let us remember that in solid state physics the energy spectra of electrons are usually pictured as the curves of electron energy dependence versus their momentum  $p$  or their wave number  $k$ , associated with the momentum via the relationship

$$p = h k \quad (15)$$

Those dependencies are plotted for each energy band, which arises from discrete levels of atoms or molecules due to their interaction.

Because of translational symmetry, the dependence of energy  $E(k)$  appears to be a periodic function, with periods equal to vectors of the reciprocal lattice. Because of that, the graphs in Figure 25 are reduced to the first



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